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Highly Reduced Carbene Complexes: Formation of an Alkoxymalonate
by Coupling of Carbon Dioxide with the Nucleophilic Carbene
in $[\text{Cr}(\text{CO}_4)=\text{C}(\text{OMe})\text{Ph}]^{2-}$

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Abstract. Reduction of a mixture of cis and trans $[\text{Cr}(\text{CO})_4(\text{PBU}_3)\{\text{C}(\text{OMe})\text{Ph}\}]$ (3) with 2.0 equiv. of potassium naphthalenide leads to formation of a highly reduced complex with carbonyl absorptions at 1859(s) and 1737(s) cm^{-1} , consistent with formation of the dianionic carbene complex $[\text{Cr}(\text{CO})_4\{\text{C}(\text{OMe})\text{Ph}\}]^{2-}$ (1^{2-}). A crystalline salt of 1^{2-} can be obtained by 18-crown-6 complexation of the K^+ counterion of samples prepared by reduction of trans- $[\text{Cr}(\text{CO})_4(\text{PCy}_3)\{\text{C}(\text{OMe})\text{Ph}\}]$ (4). The proposed formulation is supported by an unprecedented bis-carboxylation of the carbene ligand in 1^{2-} to give the unusual methoxy-malonate $\text{K}_2[\text{Ph}(\text{MeO})\text{C}(\text{CO}_2)]_2$ (K_25 , 82%), characterized by $\text{H}^+/\text{CH}_2\text{N}_2$ esterification to give $\text{Ph}(\text{MeO})\text{C}(\text{CO}_2\text{Me})_2$ (6) in 85% yield. The malonate K_25 can be prepared directly from readily available $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OMe})\text{Ph}\}]$ (2) in a single pot in 53% overall yield.

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Fischer carbene complexes¹ can be described as complexes of singlet carbenes with transition metal centers in which σ -donation from an sp^2 orbital is counterbalanced by π -donation into a vacant carbon p-orbital (Scheme I).^{1,2} In the archetypical carbene complexes of the group 6 metals the carbene replaces an isolobal CO in a zero valent hexacarbonyl to give a complex $[M(CO)_5\{C(ER_n)R'\}]$ ($M = Cr, W$; ER_n = heteroatomic substituent such as an alkoxy or amino group; R' = alkyl or aryl group) whose reactivity is dominated by the electrophilicity of the carbenoid carbon.¹ We recently became intrigued by the possibility that π -accepting heteroatomic carbenes might form stable complexes in which they replaced a CO within a carbonylmetalate such as $[Cr(CO)_5]^{2-}$, and by the possibility that the increased back-donation to the unsaturated carbon would then change the carbenoid carbon into a nucleophilic center (like the unsaturated carbon in a Schrock alkylidene complex³). We now wish to report (Scheme II) that dianionic carbene complexes such as $[Cr(CO)_4\{C(OMe)Ph\}]^{2-}$ (1^{2-}) are synthetically accessible, and that the anticipated *Umpolung*⁴ does induce a fundamentally new reactivity pattern. This is exemplified by the facile reaction of 1^{2-} with carbon dioxide to give the previously unknown malonate $K_2[C(OMe)Ph(CO_2)_2]$ via an unprecedented carbon dioxide/carbene coupling.

The synthesis of 1^{2-} utilizes a strategy similar to that which we have used to prepare phosphine,⁵ arene,⁶ and cyclopentadienyl⁷ substituted carbonylmetalates - one CO of the neutral carbene complex $[Cr(CO)_5\{C(OMe)Ph\}]$ (2) is replaced with an alkyl phosphine,⁸ and the substituted complex is reduced with an alkali metal naphthalenide at $-78^\circ C$. Low valent Cr complexes with π -acceptor ligands tend to obey the 18-electron rule and we anticipated that electron transfer would lead to phosphine loss and give a dianionic carbene complex.

Initial experiments utilized a mixture of *cis*- and *trans*- $[Cr(CO)_4(PBu_3)\{C(OMe)Ph\}]$ (3) prepared in 61 % yield by PBu_3 substitution of 2.⁸ Solution IR data suggested that potassium naphthalenide reduction (2.0 equiv of a 0.2 M THF solution) of 3 (0.72 g, 1.48 mmol in 30 mL THF) at $-78^\circ C$ resulted in formation of the desired dianionic carbene complex, since the carbonyl absorptions of the starting material

at 1881(vs) and 2020(s) cm^{-1} were replaced by absorptions at 1859(s) and 1737(s) cm^{-1} consistent with the formation of a highly reduced carbonyl complex. Attempts to isolate this anion by complexation of the K^+ with 18-crown-6 (18-C-6) or Kryptofix-222¹⁰ have been unsuccessful, but we have been able to obtain solid, crystalline salts by replacing 3 with trans- $[\text{Cr}(\text{CO})_4(\text{PCy}_3)-\{\text{C}(\text{OMe})\text{Ph}\}]$ (4).⁹ Naphthalenide reduction of an orange-red solution of trans-4 (1.14 g, 2.03 mmol) gave a dark red-brown opaque solution, from which 18-C-6 (1.07 g, 4.06 mmol) precipitated a purple solid at room temperature. This could be obtained as dark purple rectangular cubes by concentration of a filtered THF solution - these crystals would not redissolve in THF, but when dimethoxyethane (DME) was added (to dissociate the K^+ /18-C-6 complex) the resulting solution had an IR spectrum containing bonds at 1861(vs) and 1730(s) similar to those of the freshly reduced THF solution. This suggests that the crystals contain $[\text{K}(18\text{-C-6})]_2-[\text{Cr}(\text{CO})_4\{\text{C}(\text{OMe})\text{Ph}\}]$ ($[\text{K}(\text{DME})]_2$ 1, 1.02 g \approx 57%) although we have not yet obtained analytically pure samples.

The dianion 1^{2-} would be the most highly reduced carbene complex reported to date. Krusic has examined alkali metal reductions of Fischer carbene complexes¹¹ in which, for example, 2 undergoes a one electron reduction to give unstable $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OMe})\text{Ph}\}]^-$ (2^-), but does not add a second electron, presumably because the π -acceptor CO ligands are tightly bound (this emphasizes the importance of the non- π -acceptor RR_3 ligand in the reduction of 3 and 4). The only other reports of carbene complexes containing anionic metal centers are those of Winter, in which reduction of iodide precursors leads to highly reactive anionic carbene complexes of the type $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CRR}')^-]$ ($\text{M} = \text{Mo}, \text{W}$), containing zero valent metals.¹²

Our formulation of 1^{2-} is supported by the nucleophilic reactivity of the carbene ligand, as established by the reaction of K_21 with CO_2 . This was selected for study because CO_2 is not prone to single electron transfer reactions with highly reduced transition metal complexes,¹³ and we have now observed that excess CO_2 reacts readily with a solution of 1^{2-} (prepared from 0.72 g, 1.48 mmol of 3) at -78°C . The solvent was removed under reduced pressure and CH_3OH added to the washed

(hexane) orange residue to give a white solid and an orange solution. The solid was collected by filtration to give 0.35 g (1.22 mmol \approx 82%) of spectroscopically pure $K_2[Ph(MeO)C(CO_2)_2]$ (**K₂5**).¹⁴ This material was characterized by a conventional diazomethane esterification of the freshly prepared acid to give $Ph(MeO)C(CO_2Me)_2$ (**6**)¹⁵ in 85% yield after chromatography. Neither **K₂5** nor **6** have been previously reported, and methoxy-substituted malonates and malonate esters would be difficult to synthesize by conventional deprotonation of malonate diesters.

The bis-carboxylation of **1**²⁻ is unique, and the mechanistic details of the reaction remain unclear. The reaction most probably, however, involves an initial carbon dioxide/carbene coupling similar to that reported by Bergman,¹⁶ (in which CO₂ addition to an electron rich iridium methylidene complex leads to a metalloheterocycle), but in our system the initial coupling product is still so electron rich that the carbene-derived carbon adds a second CO₂ to form a second C-C bond. Carbyne chemistry provides a second model for the initial CO₂ addition in Fischer's report of metalloheterocycle formation by CO₂ addition to an anionic carbyne complex,¹⁷ and the only other report of a reaction of CO₂ with a carbene or alkylidene complex involves a reaction manifold complementary to Scheme II; Schrock has briefly stated that $[Ta(=CHCMe_3)(CH_2CMe_3)_3]$ gives bis-*t*-butylallene with CO₂¹⁸ in a reaction which is probably driven by the oxophilicity of the high valent Ta.

Our observation that **1**²⁻ is synthetically accessible and can be bis-carboxylated significantly extends the known reactivity of Fischer carbene complexes. The carboxylation is an interesting addition to the reactions of carbene complexes with potential applications in organic synthesis,¹⁹ and we have already established that **K₂5** can be prepared from readily available **2** in a single pot (without isolation of **3**) in good (53%) overall yield. The synthetic implications of this reaction are currently being explored in our laboratories.

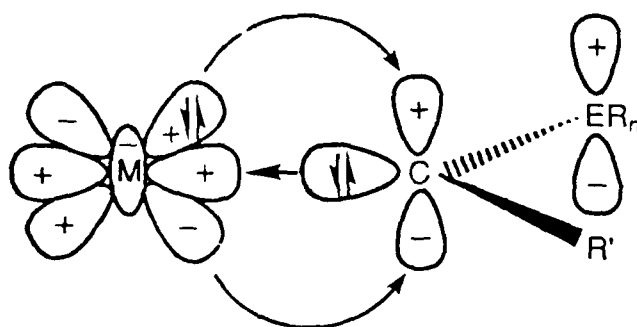
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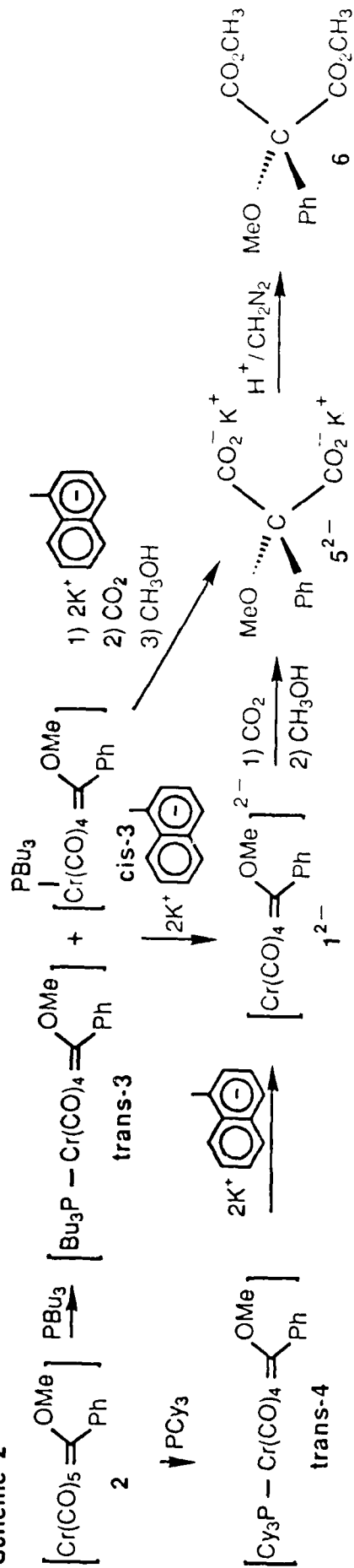
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9. This trans complex has not been previously reported, but is readily prepared from **2** in 45% yield by Fischer's method.⁸ IR (THF, ν_{CO} only) 2020 (vw), 1939 (w), 1902 (vs), 1889 (vs) cm^{-1} . ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 300 MHz), δ 7.07 (m, 5H, CH), 3.88 (s, 3H, OCH_3), 2.04-1.09 (m, 33H, PCy_3). Anal. Calcd for $\text{C}_{30}\text{H}_{41}\text{CrO}_5\text{P}$: C, 63.82; H, 7.32. Found: (Dornis und Kolbe, Mulheim an der Ruhr, BRD): C, 63.73; H, 7.43. The cis isomer can be isolated under milder conditions: Werner, H.; Rascher, H. Inorg. Chim. Acta. **1968**, 2, 181.
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14. IR (nujol mull, selected) 1611 (carboxylate); ^1H NMR (D_2O , 300 MHz) δ 7.56-7.35 (m, 5H, C_6H_5), 3.26 (s, 3H, OCH_3); ^{13}C NMR (D_2O + $\text{CO}(\text{CD}_3)_2$, 75.45 MHz, multiplicities from gated spectra) δ 176.14 (s, $2\text{CO}_2\text{K}$), 139.62-127.32 (c, C_6H_5), 90.90 (s, quaternary C), 53.07 (s, OCH_3).
15. IR (selected, neat) 1746 (ester $\text{C}=\text{O}$); ^1H NMR(CDCl_3 , 300 MHz) δ 7.55-7.35 (m, 5H, C_6H_5), 3.79 (s, 6H, $2\text{CO}_2\text{CH}_3$), 3.41 (s, 3H, OCH_3) $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.45 MHz, multiplicities from gated spectra) δ 168.34 (s, $2\text{CO}_2\text{CH}_3$), 134.69 (s), 128.84 (d), 128.23 (d), 123.33 (d) (C_6H_5), 86.36 (s, quaternary C), 54.50 (q, OCH_3), 53.01 (q, $2\text{CO}_2\text{CH}_3$). Exact mass calcd for $\text{C}_{12}\text{H}_{14}\text{O}_5$: 238.0841. Found: 238.0837.
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Scheme 1: Coordination of the Ligand in a Fischer Carbene Complex; E = O, N or S.



Scheme 2



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